

COLORING MATTERS

AND

CHEMICALS

PHILADELPHIA
UNIVERSAL EXHIBITION

COLORING MATTERS

AND

CHEMICALS

A. POIRRIER

PARIS

PARIS
IMPRIMERIE CENTRALE DES CHEMINS DE FER
A. CHAIX ET C^{ie}

RUE BERGÈRE, 20, PRÈS DU BOULEVARD MONTMARTRE

1876

A. POIRRIER

PARIS

Medal of honor,	London	1862
Gold Medal,	Paris	1867
Diploma of honor,	Lyon	1872
Diploma of honor,	Vienna	1873

Established in 1830. A. POIRRIER, head of the Firm since 1858, with CHAPPAT, junior, as partner up to 1868.

Works at SAINT-DENIS (Seine)

300 Workmen

12 Steam Engines, representing 100 horse power

14 Steam Generators — 600 horse power

Offices, 49, rue d'Hauteville.

*To the Members of the Jury of the Universal
Exhibition of Philadelphia.*

We lay before the Jury a few memoranda on the improvements or inventions that we have made in our industry, and on the advantages which have resulted therefrom, so far as concerns *economy in the cost price, improvement of qualities, and diminution of price of a precious medicine : Iodine.*

We were fortunate enough to be the *first*, with the help of able chemists, Messrs. Lauth, Bardy, Baubigny, Morel, to obtain practically, at our Works of Saint-Denis, the production of :

1° *Methylaniline, the varieties of Methylaniline violet, and of benzylated Methylaniline violet, called « PARIS VIOLET ».*

2° *Methylaniline night green.*

3° *We have been able to suppress the use of Iodine in the manufacturing of these products.*

4° *We have established at our Works the manufacture of sulphurated products called « CACHOU DE LAVAL » discovered by Messrs. Croissant and Bretonnière ; giving Shades unaffected by exposure to air, of an easy application and produced at a very low price.*

INVENTIONS AND IMPROVEMENTS

I

Practical production of Methylaniline, and varieties of Paris violet, without Iodine.

The Hofmann varieties, of violet, Ethyl and Methylaniline violet were not long, owing to their brilliancy, in supplanting other descriptions of violet such as bichromate violet and phenyl-rosaniline violet.

But the manufacturing of this fine coloring matter necessitated the use of considerable quantities of Iodine, the price of which soon reached from 20 to 100 francs a kilogram.

Under those circumstances the cost price of the different sorts of Hofmann violet remained very high, and they were sold at 200 francs a kilogram, when we succeeded, in 1866, with Mr. Bardy's assistance, in producing practically methylaniline free of Iodine and the different sorts of methylaniline violet.

Until then they had only been able to obtain methylaniline in laboratories, it being prepared by the reaction of iodide of methyl on aniline.

After a great many searches and trials, which were often unfruitful, we had recourse, with success, at our Works, to the process made use of by the learned professor Berthelot, recommended by him, for the introduction of alcoholic radicals into ammoniac, by heating under high pressure an aniline salt “ the chlorhydrate ” and methyl-alcohol.

We transformed the methylaniline obtained, into violet, by causing iodine and chlorate of potash to react at a low temperature.

Shortly after, Mr. Lauth, who had obtained in 1861 a methylaniline violet, brought us a process for oxydation of methylaniline, by chloride of copper, much more advantageous in the cost price than the one above mentioned.

Finally we were able to obtain the bluest and most brilliant sorts of violet by the reaction of chloride of benzine on methylaniline violet.

The advantage of these different sorts of benzyled violet is that they can be fixed on the animal fibre by dipping them in a bath slightly acidulated, without altering its brilliancy.

At the present moment we sell the bluest varieties of methylaniline violet and benzyled methylaniline violet at prices from 30 to 45 francs a kilog.

In consequence we have been able to solve, for the different varieties of violet, the double problem of cheap PRODUCTION and IMPROVEMENT OF QUALITY (1).

(1) See annexes.

Production of Methylaniline Green free of Iodine.

II

SUBSTITUTION OF THE METHYLANILINE VIOLET TO THE ROSANILINE FOR THE MANUFACTURING OF NIGHT GREEN.

The suppression of iodine in the manufacture of the varieties of violet led us naturally to look for the same progress in the manufacture of night green which was obtained in same time as the varieties of Hofmann violet, by the reaction of alcoholic iodides on rosaniline; it can even be said that there was in this a more important point to be attained, as green is consuming quantities of iodine so much the more important as this body forms the constitutive part of green.

The first improvement realized in that order of ideas consisted in manufacturing night green by the action of methyl iodide on the different varieties of methyl aniline violet, and no longer on rosaniline; in fact this last substance consumes more iodide, to be converted into green, than the methylaniline violet, as the latter already contains a certain proportion of alcoholic radicals which one proposes to introduce by the action of iodides.

Ever since the end of 1868, we have exclusively employed methylaniline violet for the manufacture of green.

III

MANUFACTURING OF NIGHT GREEN WITHOUT IODINE.

When we had introduced in the manufacturing of the varieties of violet the use of chloride of benzyl, being struck with the analogy which exists between this agent and the alcoholic iodides, we made numerous efforts to replace them by the same in the manufacture of green; such efforts were fruitless, we were obliged to look for another product.

Mr. Baubigny, in our own laboratory, having taken up again and modified the trials which we had at divers times made, found the way of replacing iodide of methyl by *nitrate of methyl*, which, in the action exercised on the methylaniline violet, determines the formation of a large quantity of green (1).

This manufacture has been in operation in our Works since the end of the year 1871, and the long pointed green crystals of a metallic lustre were already to be seen at the Exhibition of Lyons in 1872. No manufacturer had up till then delivered night green in so pure a state, and it is about the only one in demand now in the market.

(1) By comparing the cost price of methyl iodide (100 francs), with nitrate of methyl (4 francs), it will be seen what considerable advantage there was in employing this latter substance.

We must state that nitrate of methyl which by its action on methylaniline violet, produces considerable quantities of green, gives only little, or none at all when reacting on rosaniline.

Owing to the measures of precaution which had been taken, the manufacture of nitrate of methyl presented in itself no danger. Mr. Morel who superintended this fabrication produced more than 50,000 kilograms without any accident, when a man approaching a light to the product in evaporation, caused the terrible accident which is known.

The road being opened, other manufacturers managed to replace nitrate by chloride of methyl, which we do ourselves to-day.

We sell 400 francs the kilogram the varieties of light crystallized green much purer than the varieties of iodide green which were sold 800 francs the kilogram, so that

We have solved for the green, as well as for the violet, the double problem of ECONOMY in COST PRICE and IMPROVEMENT of QUALITY (1).

IV

New process of dyeing wool night green.

Seeing the cheapness in the production of night green, we endeavoured to extend the applications of it. If the

(1) See Annexes.

silk and cotton dyers had succeeded without difficulty in employing green; it had not been the same with wool dyers, this fibre not having the same affinity for green as for other aniline colors.

Dyes in alkaline baths, after the manner of Nicholson's blues, gave but poor results; and it was necessary to find a new and special process.

This was successfully realized by Mr. Lauth, in previously mordancing the wool in an acid bath of hyposulphite of soda; the sulphur in emulsion in the water sticks to the fibre and enables it to attract the green; thus you can obtain shades of incomparable intenseness and beauty. (1)

V

New mode of manufacturing sulphuretted productions called "Cachou de Laval"

We call the special attention of the Jury to the sulphuretted productions discovered by Messrs. Croissant and

(1) We call to mind that Mr. Lauth in 1869 made also known a process of dyeing cotton in aniline black by means of peroxide of manganese; this chemical is based on a principle analogous to that which has allowed this chemist to bring into the trade the discovery of aniline black in printing (sulphide of copper).

Bretonnière who have ceded to us the right of working them and which we call “*Cachou de Laval*”

These products obtained by the reaction of alkaline sulphides on organic matters, produce tints of various shades according to the fixative agents employed, from the buff tint to the drab; and enjoy this triple property of giving tints of a *great stability to the air and washing with soap*, of being *very cheap* and of *simplicity of employment*; these products in fact stick to the vegetable fibres simply by passing them through a bath of water.

They are now actually much appreciated for sundry applications, particularly for articles of drill, cotton velvets and mixed fabrics of wool, cotton, etc., which are so difficult to dye by the ordinary process.

VI

Improvements made in our divers manufactures.

ROSANILINE AND ITS DERIVATIVES, BLUES, SAFFRANINE, ARCHIL,

EXTRACT OF ARCHIL, EOSINE, ETC.

The improvements we have realized in the manufacture of rosaniline and its derivatives, are less important than those we have made known for obtaining varieties of violet and green, but they are not the less real.

In varying the proportion of the divers alkaloids which enter into its composition we obtain as we want, the divers species of rosaniline which we destine either to the use of dyeing, or to such and such transformation.

According to the blue we wish to obtain, we also react the said alkaloids in variable proportions on a determined rosaniline.

The blue which must be used in alcóholic dissolution is not of the same composition as that destined to be combined with sulphuric acid.

Finally this manufacture of sulphoconjugate blues is perfectly regular, and we obtain as we want the first, second or third acid combination, according to the application to which these productions are destined.

Our blues are obtained under conditions of pureness and cheapness which no other mark can come up to, and are well known and appreciated as our other productions, particularly as our violet and green colors, by American consumers.

All necessary arrangements, such as apparatuses, installations, and manipulations, have been made to avoid the accidents which might take place in the manufacture of rosaniline, either as regards public health, or as regards the health of the workmen, and, up to this date, we have had no accidents to bewail.

Moreover our workmen are placed under special care, that is to say : regular medical visits, baths, etc.

The manufacture of rosaniline and blue colors is directed with the greatest sagacity and perseverance by Mr. T. Robatel.

The so very delicate manufacture of safranine, is perfectly well managed by Mr. Luizet, as well as our manufacture of archil, extract of archil, and cudbear, which continues to increase ; besides our sales in France, the export orders for extract of archil, more particularly for the United States, are so important, that our manufacture, which has been doubled in one year, is still insufficient.

We have commenced to manufacture eosine and the several matters necessary for its production, resorcine, and phthalic acid, and we are beginning to supply trade with this coloring matter.

We must here mention that in the course of the years 1868 and 1869, we produced, by original processes, a certain quantity of green derived from benzine and from dibenzyl-aniline ; and that the development of this manufacture was stopped owing to the use of considerable quantities of alcohol necessary to dissolve this new coloring matter.

The increased cost price resulting from the employment of alcohol, has caused this green to be of less interest compared with the varieties of methylated green soluble in water ; and made us give up this manufacture (1).

(1) See annexes.

RESULTS OF OUR IMPROVEMENTS AND DISCOVERIES.

I

Suppression of Iodine in the manufacture of coloring matters.

Advantage, from a sanitary point of view, of this suppression and of the substitution of the varieties of methylaniline violet to rosaniline.

The production of iodine is the most limited; it is only made in France on the coast of Brittany, in Scotland and Ireland.

The quantities produced by France and England are of about the same importance : about 75,000 kilograms for each of these countries; but, on account of the bad state of the atmosphere, this amount has decreased of late years to 100,000 kilograms for the consumption of the whole world.

The manufacture of violet and green colors with alcoholic radicals arrived at such a development that

the demand for iodine for their production, amounted to not less than 50,000 kilograms during 1871; this quantity presents one half of the total production.

Moreover the consumption of iodine for medical purposes continues to increase, so that this ingredient which in 1862, when it was only employed pharmaceutically, and was not worth more than 20 francs per kilogram, attained the price of 100 francs.

Such prices became an inducement to fraud, and it is known to us that attempts were made to give the bromide an appearance of iodide of potassium, so that it might be offered as such to the trade, and this bromide was given to more than one patient in the place of iodide.

But owing to our discoveries, the use of iodine in the manufacture of coloring matters extracted from coal being entirely suppressed, iodine soon lost its value and from the price of 100 francs, which it was worth in 1872, fell to its present price of 25 francs; the fraud above stated ceased, the difference of price not being sufficient between the two.

Our new processes have not only contributed to have a good influence from a sanitary point of view, by restituting to pharmaceutical purposes 50,000 kilograms of iodine; they also contribute in reducing on a large scale the use of arsenic acid; an advantage which is not less important for public health.

In fact, in manufacturing violet and green colors by our process without making use of rosaniline; we reduce the consumption of this last named product, which

is always prepared by means of arsenic acid, on account of the considerable economy in its cost price.

Now, in spite of every care and precaution, the handling of large quantities of arsenic acid is dangerous; therefore the more its employment is limited, the less danger there is.

From this point of view we believe we have rendered a real service to public health by reducing to a very great extent the employment of rosaniline and in consequence that of arsenic acid.

II

Cheapness, improvement in quality.

By our discoveries we have been able to reduce the selling price of our violet and green colors to the enormous proportions which we have above stated. The varieties of Hofmann violet were sold at 200 francs, we sell to day violets of Paris from 30 to 40 francs; the green colors fell from 800 to 100 francs; and all the violet and green colors at present offered to the trade, are manufactured according to our system. In spite of this competition our production has always been increasing on account of the lowering of our prices (1).

(1) See annexes.

ORGANIZATION, DIVISION OF LABOUR

I

In pointing out the improvements and inventions in the different branches of our manufacture, the share which each of our cooperators has taken in this work has been shown; it will therefore suffice to sum up the preceding lines to make known what organization we have adopted in our firm.

A. Poirrier has the general management of the production and sale. He is assisted in the second part of his duties by a commercial director.

Four special chemists with foremen under their orders direct each of the manufactures.

The sale is effected by means of numerous agents scattered over the centres of consumption in all parts of the globe; each of these agents has a dépôt of products of every description (and they are numerous) which they deliver for our account to the consumers in their district.

II

Intercourse with the cooperators. Participation.

Besides their fixed salaries, all those who help us in our manufacture, chemists, foremen and workmen who have remained at least two years in our service participate in the profits.

The salesmen participate equally in the profits, or are paid a commission of so much per cent., on the amount of business done in the district which they work.

To stimulate the zeal of these agents and keep them continually informed of the improvements, we have travellers who visit them once or several times a year, and with them the consumers; we must here say that Mr. Hardy, our assistant for the last eighteen years about, has contributed, by his activity and perseverance, to a great extent, in causing our productions to be appreciated, and in introducing them to French and foreign consumption.

The chemists participate in the profits on the manufacture directed by them; this share increases when they effect an important improvement in their manufacture.

The foremen and workmen receive, after the annual inventory is completed, a share in the profits, in proportion to the salary paid to them since their employment at our factory.

On an average of 300 workmen employed in our factory,

there were, in 1875, 110 participants. The share which was paid them on the profits of 1875 represented for some of them one fifth of their annual salary; for the less favored, that is to say those who had only been employed two years at the Works, the fifteenth part.

Instead of paying them this amount in money, we gave them savings-books, where the capital cannot be touched before a stipulated delay sufficiently long for the holders to be able to see, at its expiration, their savings increased either by the payment of a new participation in the profits, or by their own economy.

The total portion of the different participants is about 40 0/0.

Tour improvements and discoveries have procured us :

The gold medal — PARIS 1867.

Diploma of honor — VIENNA 1873.

And to our assistants :

Mr LAUTH. — *Gold medal* — PARIS 1867.

— *Diploma of honor* — VIENNA 1873.

Mr BARDY. — *Silver medal* — PARIS 1867.

— *Diploma of honor* — VIENNA 1873.

Mr BAUBIGNY. — *Cooperation medal* — VIENNA 1873.

Mr MOREL. — » » — » »

ANNEXES

EXTRACTS FROM THE REPORTS
OF THE
MEMBERS OF THE INTERNATIONAL JURIES
Of the Exhibitions of
PARIS 1867, AND VIENNA 1873
ON THE DISCOVERIES AND IMPROVEMENTS EFFECTED
BY
M^r A. POIRRIER AND HIS COOPERATORS

*Mr. Berthelot's Report on the Paris Universal Exhibition
of 1867.*

At the present moment, this method of closed chambers begins to occupy the attention of manufacturers, the processes of pure science are being appropriated to industry with alterations to suit its own system. Thus, for instance, it has been proposed to saponify fat substances by pure water at a temperature of about 200°.

If the enormous pressure produced under these circumstances has obliged to give up the reaction of water on fat substances employed in all its simplicity, it has however succeeded in making this reaction contribute to the saponification of neutral fatty substances, by employing, at the same time, with the water, a small quantity of lime, which allows to operate at a lower temperature and under less pressure, but always with the use of closed chambers.

Messrs. Poirrier and Chappat were even bolder when they made use of closed chambers for the preparation of methylaniline, by the reaction of methyl-alcohol upon chlorhydrate of aniline, and in conformity with a scientific method made known by Mr. Berthelot for the production of organic alkalis.

The methylaniline prepared by their system and the fine violet coloring matter produced therefrom are shown at the Exhibition.

These first attempts may be looked upon as the prelude of discoveries that commerce may look forward to in a new and fruitful line.

Mr. Balard's Report on the Paris universal Exhibition of 1867.

Mr. Lauth, whose name is frequently to be found in this account of discoveries relating to new colors, oxydising since 1861 methylaniline as pure as it can be practically furnished, had obtained a new violet, the manufacture of which he was obliged to renounce on account of the difficulty in preparing the raw material.

But these studies, resumed by Messrs. Poirrier and Chappat, with the important assistance of their chemist, Mr. Bardy, have recently produced the anticipated results.

These experienced manufacturers have not only succeeded in making methylaniline at an extremely low cost, by imitating a process which had been used by Mr. Berthelot for obtaining Mr. Hofmann's alcoholic ammoniacs, but they have also succeeded, by means of an appropriate oxydising action, in transforming this substance into an entirely new violet; — into methylaniline violet.

This violet which differs in some of its properties from that obtained from rosaniline, as from its nature it necessarily would, since it has been produced with the purest aniline possible to obtain practically, recalls to mind, however, its brilliancy and beauty, but in a lesser degree.

In 1861, Mr. Lauth brought, in his turn, a most useful assistance to the manufacture on a large scale, of the product he had discovered.

By the introduction of heat to assist the oxydising action of air and other more powerful oxydising agents, he was able to produce with one hundred parts of methylaniline, more than forty parts of a violet obtained under most economical conditions, and of which the employment already begins to spread itself in France and abroad.

Report of Dr. A. W. Hoffmann, George de Laire and Charles Girard, on the Paris Universal Exhibition of 1867.

As may be seen, the process patented by Messrs. Poirrier and Chappat is double.

It comprises, on the one hand, the manufacture of matters derived from the ethyl and methyl of aniline; and on the other, the transformation of these secondary monamines into violet coloring matters.

The method they adopted to produce methyl- and ethyl-aniline, is that indicated by Mr. Berthelot for producing monamines, in a general way, with alcoholic radicals.

This is a new example of the adoption by commerce of scientific methods : and remarkable to relate, of all of those which had been employed for the preparation of methylic and ethylic alkalis, the latter, which seemed the least practical in the laboratory, is the only one which has become practical.

Mr. Ad. Wurtz's Report on the Vienna Exhibition of 1873.

Thus, by the united efforts of Messrs. Ch. Lauth and Bardy, and thanks to the inventive spirit and intelligent direction of Mr. Poirrier, the discovery of the direct transformation of methylaniline into violet has passed from the state of experiment into that of practical use, a result doubly happy from an

economical and sanitary point of view, for, if it permits the suppression of a costly agent and of which the variations in price were dominated by the coalition of the producers, it has also procured the advantage of restricting the unwholesome manufacture of Rosaniline.

Mr. Ad. Wurtz's Report on the Vienna Universal Exhibition of 1873.

It is known that the vapour from Nitrate of Methyl explodes when it is over-heated. The employment of such a dangerous substance has not been accepted without hesitation. However, by the care with which its preparation has been surrounded and the precautions taken at Mr. Poirrier's factory, which an unfortunate accident baffled some months ago, this preparation became a current manufacturing operation, carried out with great regularity.

The preparation of Nitrate of Methyl was executed very regularly and the produce amounted to 150 0/0 of the wood spirit used ; at Mr. Poirrier's works, making two operations per day, with a battery of twelve globes, 80 to 84 kilograms of *Nitrate of Methyl* were produced.

Mr. Ad. Wurtz's Report on the Vienna Universal Exhibition of 1873.

We wish to call attention to some attempts made by several chemists to produce green coloring matters by the aid of divers benzylic derivatives. Messrs. Ch. Lauth, Bardy, and Poirrier have tried to obtain directly such matters, by depriving dibenzylaniline of hydrogen.

The product obtained, not being easily soluble in alcohol, they have given up its use.

*Mr. E. Kopp's Report on the Vienna Universal Exhibition
of 1873.*

By the action of chloride of benzyle, Mono- and Dibenzylaniline were prepared, also Benzyl-toluidine, in a similar manner.

By causing to react separately on these substances, especially on Benzylaniline or their mixtures, oxydising or dishydrogenising substances such as diluted nitric acid, chloride of copper, etc., Messrs. Poirrier, Bardy and Lauth obtained with the simultaneous formation of Benzoic Aldehyde (true Oil of Bitter Almonds) some fine green colors, called by them Paris Green Dyes. But as these substances were not soluble in water and required for dyeing purposes, considerable quantities of alcohol, which rendered their employment very costly, they could not withstand the competition of other Aniline Green Dyes, and their manufacture was very soon abandoned.

But the success of the discovery of Mr. Baubigny, chemist to Mr. Poirrier, was quite different; this discovery consisted in substituting in the transformation of violet into green colors, the costly Iodide of Methyl by Nitrate of Methyl, relatively cheap and only worth 4 francs a kilog.

In fact, this substance reacting on the violet of methyl, gives a considerable quantity of a magnificent green soluble in water, while rosaniline gives none or very little.

Although it is not by any means an inoffensive substance, and as its preparation and manipulation requires the greatest precaution, the consumption of Nitrate of Methyl soon became very considerable.

Thus, in Mr. Poirrier's factory, Mr. Morel produced, from 1871 to 1873, without any accident, more than 20,000 kilogs. of Methyl; the whole of which was used for the manufacture of Green dye.

It is necessary nevertheless to take the greatest care, especially never to approach the workshops where nitrate of methyl is made or being used, with a light. The terrible accidents which occurred some years ago at Rübeland in the Hartz mountains and last year at Mr. Poirrier's Works at Saint-Denis will be easily remembered.

M. Kopp's Report on the Vienna Universal Exhibition.

SAFFRANINE. — Every difficulty of this delicate preparation has been surmounted by the manufacturers. Saffranine is found in the chlorhydrate state, in the form of a paste or in a crystalline powder.

The finest qualities produced are made by Messrs. Lotz, Durand and Huguenin-Geigy of Basle and Poirrier of Paris.